

Basis Set and Correlation Effects in the Calculation of Accurate Gas Phase Dimerization Energies of Two M_2^+ to Give M_4^{2+} (M = S, Se)

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ABSTRACT: The dimerization energies of two M_2^+ to give M_4^{2+} (M = S, Se) were calculated. They depend strongly on the size of the basis set and the correlation method used (ranging from 217 to 522 kJ/mol, M = S) and, therefore, a systematic study of basis set and correlation effects was performed [MP2, MP3, MP4(SDQ), CCSD, CCSD(T)]. The introduction of a second set of polarising d-functions caused a significant reduction of the dimerization energies, but neither of the above limits is reached by the MP_n ($n = 2, 3, 4$) theory, even with the largest basis sets [cc-pVQZ]. However, convergence was achieved by CCSD(T), compound methods or hybrid HF/DFT calculations employing flexible basis sets [e.g., CCSD(T)/cc-pV5Z, CBS-Q or B3PW91/6-311+G(3df)] and revealed an average dimerization energy of 261 (199) kJ/mol for sulfur (selenium), $\Delta_r H^{298}$ ($2S_2^+ \rightarrow S_4^{2+}$) is 257 kJ/mol. In the selenium system the dependence on basis set and correlated method was less pronounced.
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Introduction

With the exception of O_2^+ , all the known salts containing homopolyatomic cations of group 16 are diamagnetic multicharged species: for example, S_n^{2+} $n = 4, 8, 19$; Se_n^{2+} $n = 4, 8, 10, 17$; Te_n^{2+} $n = 4, 6, 7, 8, 10$; Te_n^{4+} $n = 6, 8$.^{1,2} Although the existence of singly charged colored, sulfur homopolyatomic radical cations in solution at low concentration has been well established, including blue S_5^+ , and what is probably S_7^+ ,³ no isolable salt of a heavier chalcogen radical cation has been synthesized so far. In our efforts to understand the exclusive formation of diamagnetic dications we are currently performing a series of thermodynamic lattice potential energy and Born–Fajans–Haber cycle calculations to model the solid state behavior of the homopolyatomic chalcogen cations.⁴ Accurate gas phase dimerization energies of the respective species are needed as an input and therefore the dimerization reaction of 2S_2^+ to give S_4^{2+} was examined computationally in 1994 by Grein and Sannigrahi. They found a dimerization energy of 443 kJ/mol (ROHF/6-31G*).⁵ From our investigations of the solid-state thermodynamics of this system,⁴ we realized that this dimerization energy must be too high. We, therefore, undertook a new theoretical study of the $\text{M}_2^+/ \text{M}_4^{2+}$ ($\text{M} = \text{S}, \text{Se}$) system, and found dimerization energies varying widely at different levels of theory. Consequently, we initiated a systematic study of correlation and basis set effects for these reactions. To probe the reliability of the calculations, the experimentally accurately determined first ionization potential⁶ of disulfur S_2 was calculated and included in the investigation.

The ionization potential of triplet S_2 had been studied theoretically as part of the G1 and G2 molecule set as a test for the reliability of the Gaussian-1 and Gaussian-2 theories^{7,8,20} as well as the CBS-Q method.^{19a} Theoretical calculations of the S_4^{2+} dication were reported as early as 1979 by Fukui and coworkers.⁹ They, as well as later groups,^{10–14} were able to computationally reproduce the square planar, D_{4h} -symmetric geometry of S_4^{2+} found experimentally by Passmore et al.^{4,15}

Computational Details

All calculations have been performed on Pentium II personal computers (233–333 MHz, 128 MB RAM) using the Gaussian94W¹⁶ suite of programs.

All computed geometries were fully optimized at the given level of theory. A frequency calculation followed to verify its nature as a stationary point on the hypersurface, and all are true minima. Zero-point energies were included at various levels of theory, but these never caused changes in the energies of more than 3 to 4 kJ/mol. However, entropy contributions to the free energy additionally favor the gas phase dissociation of M_4^{2+} into 2M_2^+ ($\text{M} = \text{S}, \text{Se}$) at 298 K by about 50 kJ/mol. Basis set effects have been studied at the HF, MP2, MP3, MP4(SDQ), CCSD, and CCSD(T) levels of theory by calculating single-point energies using fixed geometries calculated with Becke's three-parameter hybrid exchange functional¹⁷ and the Lee–Yang–Parr gradient corrected correlation functional¹⁸—B3LYP/6-311+G*. Basis sets were used as implemented in Gaussian 94W. To model the energies near the correlation and basis set limit, Peterson's complete basis set extrapolation¹⁹ CBS-Q as well as the Gaussian-2²⁰ compound method as implemented in Gaussian94W were used.

Results and Discussion

THE DIMERIZATION ENERGY FOR THE REACTION OF 2S_2^+ TO GIVE S_4^{2+} —PART 1

All reports on the solid state geometry of M_4^{2+} ($\text{M} = \text{S}, \text{Se}, \text{Te}$)^{4,15,21,22} agree on a square planar D_{4h} symmetric structure for these dications. Therefore, we used this symmetry restriction for all calculations performed to obtain the gas phase dimerization energy. Based on estimates of the solvated energies of 2S_2^+ and S_4^{2+} (Born equation) and solution Raman spectroscopy (v.s.)^{4,15d,23} it is recognized that the published dimerization energy for the $2\text{S}_2^+/\text{S}_4^{2+}$ system of 443 kJ/mol (ROHF/6-31G*) is too high. Various levels of theory and different basis sets give dimerization energies for the $2\text{S}_2^+/\text{S}_4^{2+}$ system, which range from 250 to 522 kJ/mol, as summarized in Table I. For a given level of theory, the dimerization energies always decrease with the improved basis set. The correlated methods give substantially lower dimerization energies than those employing HF theory, and very low values are obtained from the hybrid HF–DFT theory.

THE FIRST IONIZATION POTENTIAL OF S_2

To understand the widely varying dimerization energies and to select an accurate value for the thermochemical calculations (v.s.), we initiated the systematic study of a test reaction: the ionization

TABLE I.
Computed Ionization Potentials of S₂ and Dimerization Energies of the 2S₂⁺/S₄²⁺ System Including *d*(S—S)
[in (Å)] at Various Levels of Theory.

Level of Theory	S ₂ <i>d</i> (S—S)	S ₂ ⁺ <i>d</i> (S—S)	IP of S ₂ kJ/mol	S ₄ ²⁺ (<i>D</i> _{4h}) <i>d</i> (S—S)	Δ <i>U</i> _{dim} kJ/mol
Experiment	1.889	1.824	902.7 ± 0.2	2.011 (3)	—
MP3/6-311+G*	1.912	1.833	873.4	2.051	374
MP3/6-311+G(3df)//MP3/6-311+G*			901.1		295
CISD/6-311G*	1.903	1.823	877.1	2.019	522
QCISD(T)/6-311G*//HF/6-311G*			865.4		466
QCISD/6-311+G*	1.915	1.840	869.6	2.055	396
QCISD(T)/6-311+G*//QCISD/6-311+G*			861.0		376
B3LYP/6-311+G*	1.927	1.840	933.2	2.072	337
B3LYP/aug-cc-pVTZ	1.913	1.833	924.0	2.051	280
B3PW91/6-311+G*	1.914	1.831	937.5	2.053	313
B3PW91/6-311G(2df)	1.897	1.819	925.6	2.027	254
B3PW91/6-311+G(3df)//			925.2		256
B3PW91/6-311+G*					
B3PW91/aug-cc-pVTZ//			928.0		250
B3PW91/6-311+G*					

potential of S₂. The published, very accurately determined experimental adiabatic ionization potential of S₂ (IP_{exp} = 902.7 ± 0.2 kJ/mol)⁶ is reproduced reasonably well at the ROHF/6-31G* level of theory (918.4 kJ/mol), which was employed for the original determination of the published gas phase dimerization energy.⁵ However, as shown above, the dimerization energy of 2 S₂⁺ is too high. This suggests that the good agreement of the calculated first ionization potential of S₂ at this level of theory with an experiment might have been fortuitous—various examples of the HF theory mirroring experimental properties by chance can be found in the literature.²⁴ To investigate whether this is the case here, and to obtain values for the ionization potential near the correlation and basis set limit, we calculated single-point energies for triplet-S₂ and doublet-S₂⁺ [B3LYP/6-311+G* geometries, *d*(S—S) = 1.9272 and 1.8402 Å, respectively] at the HF, MP2, MP3, MP4(SDQ), CCSD, and CCSD(T) levels of theory employing successively larger basis sets [6-311+G* to cc-pVQZ]. S₂ and S₂⁺ are well described by a single-reference treatment, as shown by the small T1 diagnostic of 0.013 and 0.015 obtained in initial CCSD/cc-pVDZ calculations, which justify the approach chosen. The major difference between the results obtained at the HF level and the

correlated levels of theory are seen in Table II. As the size of the basis set is increased, HF results decrease, although the experimental value of 902.7 ± 0.2 kJ/mol and beyond it [e.g., from 911.6 kJ/mol (6-311+G*) to 894.2 kJ/mol (cc-pVQZ)] while the MP n ($n = 2, 3, 4$) levels show an increase from below the experimental result [e.g., from 861.5 to 894.1 kJ/mol (MP2), 873.1 to 908.3 kJ/mol (MP3) and from 869.7 to 906.9 kJ/mol MP4(SDQ)]. MP3 and MP4(SDQ) increase through the experimental value. Larger basis sets in the HF calculations give rise to ionization potentials, which are too low. Therefore, the agreement between experimental determination and the ROHF/6-31G* level must be fortuitous. The best agreement between experiment and theory is found at the computationally very expensive CCSD(T)/cc-pVQZ level of theory. This method reproduces the experimental value of 902.7 ± 0.2 kJ/mol to within 0.6 kJ/mol (902.1 kJ/mol). The accuracy of the CCSD(T) calculation can be further enhanced by extrapolating the total atomic energies to the complete basis set limit [denoted CBSE(b,c) in Table II]. This procedure³¹ reproduces the experimental value exactly, for example, the ionization potential of S₂ at the CCSD(T)/CBSE(b,c) level is 902.7 kJ/mol. When the experimental³¹ zero-point energies of S₂

TABLE II.

Ionization Potential (kJ/mol) of S_2 (Experiment: 902.7 ± 0.2 kJ/mol)⁶ at the HF, MP2, MP3, and MP4(SDQ) Level of Theory Employing Different Basis Sets [B3LYP/6-311+G* Geometries, $d(S-S) = 1.9272$ and 1.8402 Å, Respectively].

Basis Set	HF	MP2	MP3	MP4(SDQ)	CCSD	CCSD(T)
6-311+G*	911.6	861.5	873.1	869.7	—	—
6-311+G(2d)	898.1	882.6	891.9	887.5	—	—
6-311+G(3df)	894.1	887.6	900.4	898.5	—	—
cc-pVDZ	906.7	873.6	884.0	879.9	879.8	874.1
cc-pVTZ	896.0	889.5	902.8	900.8	900.9	894.6
cc-pVQZ	894.2	894.1	908.3	906.9	906.7	902.1
CBSE(b,c) ³¹	893.8	894.6	908.9	907.5	907.4	902.7

(4.35 kJ/mol) and S_2^+ (4.73 kJ/mol) are included in the calculation, the ionization potential is lowered marginally by 0.38 kJ/mol. The ionization potentials as calculated with all other methods at the extrapolated basis set limit [CBSE(b,c) in Table II] only differ by a maximum of 0.7 kJ/mol from the respective value obtained with the cc-pVQZ basis set. This implies that the cc-pVQZ basis set is close to the basis set limit.

To model the ionization potential accurately, electron correlation is not the only important factor. Even at the MP4(SDQ)/6-311+G* or the CCSD(T)/cc-pVDZ levels of theory, employing a highly correlated method in combination with a moderately large basis set, the quality of the calculated ionization potentials is rather poor (869.7 and 874.1 kJ/mol vs. 902.7 ± 0.2 kJ/mol found experimentally). To obtain a thermochemically accurate value, both a highly correlated method and a large and flexible basis set have to be employed [e.g., CCSD(T)/cc-pVQZ: 902.1 kJ/mol].

THE DIMERIZATION ENERGY FOR THE REACTION OF 2 S_2^+ TO GIVE S_4^{2+} —PART 2

A similar approach as delineated for the S_2 ionization potential was chosen for the interpretation of the wide range of dimerization energies in Table I. S_4^{2+} is well described by a single-reference treatment (T1 diagnostic = 0.015; CCSD/cc-pVDZ) and, therefore, single-point energies of a reasonably well-refined geometry with increasingly more sophisticated levels of theory and larger basis sets were calculated for S_2^+ and S_4^{2+} [fixed B3LYP/6-311+G* geometries, $d(S-S) = 1.8402$ and 2.0718 Å (D_{4h} -symmetry), respectively]. The validity of this approach is established by a comparison of the dimerization energies at the fully optimized MP3/6-311+G* or MP3/6-311+G(3df)//MP3/6-311+G* (374 and 295 kJ/mol, Table I) level and the corresponding MP3/6-311+G*//B3LYP/6-311+G* or MP3/6-311+G(3df)//B3LYP/6-311+G* (375 and 299 kJ/mol, see Table III) single-point energies. Both

TABLE III.

Dimerization Energies (kJ/mol) for the $2S_2^+/S_4^{2+}$ System at the HF, MP2, MP3, and MP4(SDQ) Level of Theory Employing Subsequently Larger Basis Sets [B3LYP/6-311+G* Geometries, $d(S-S) = 1.8402$ and 2.0718 Å (D_{4h} -symmetry), Respectively].

Basis Set	HF	MP2	MP3	MP4(SDQ)	CCSD	CCSD(T)
6-311+G*	454.41	355.20	375.08	399.85	—	—
6-311+G(2d)	413.91	258.33	309.76	331.35	—	—
6-311+G(3df)	423.00	242.26	299.37	321.93	—	—
6-311G(3d2f)	417.28	231.95	291.94	314.38	—	—
cc-pVDZ	464.68	327.74	368.21	388.64	387.41	359.55
cc-pVTZ	417.17	233.83	293.01	315.00	313.59	285.95
cc-pVQZ ³²	415.74	216.78	279.12	302.83	300.65	270.98
CBSE(b,c) ³¹	414.31	213.93	276.85	300.60	298.42	268.76

calculations agree to within a few kJ/mol, indicating the presence of shallow potentials for the S_2^+/S_4^{2+} geometries. The data of the single-point calculations are summarized in Table III. They reveal a more pronounced dependence of the dimerization energy on the level of theory and the size of the basis set employed than that found for the ionization potential of S_2 . In contrast to the latter property, the dimerization energies as calculated within the MP n ($n = 2, 3, 4$) theory do not converge to a single value.

However, the underlying trend in the calculations is evident: replacing smaller basis sets by larger ones leads to a decrease in this energy, with a very pronounced decline when a second set of polarizing d-functions is introduced. Augmenting the basis sets with diffuse functions does not improve the quality of the computation. The inclusion of dynamic electron correlation by second-, third-, and fourth-order MP perturbation analysis leads to a dramatic overall decrease in the dimerization energy of 55 [HF/6-311+G* vs. MP4(SDQ)/6-311+G*] to 199 kJ/mol [HF/cc-pVQZ vs. MP2/cc-pVQZ]. The ordering of the dimerization energies follows $E_{\text{dim}}(\text{HF}) > E_{\text{dim}}(\text{MP2}) < E_{\text{dim}}(\text{MP3}) < E_{\text{dim}}[\text{MP4}(\text{SDQ})]$. Because MP perturbation theory is not variational, and MP2 is known to somewhat overestimate the electron correlation, which again is corrected by MP3 and MP4,²⁴ the values in Table III can be interpreted as follows: as the size of the basis set is increased, the HF results display an erratic variation in contrast to the results at the MP n levels, which show gradually decreasing dimerization energies reaching, in the case of MP2, a value of 216.78 [cc-pVQZ] and in the case of MP3 and MP4(SDQ) values of 279.12 and 302.83 kJ/mol [cc-pVQZ]. Accordingly, we take the latter two estimates as upper limits for the dimerization energy (<300 kJ/mol) and the presumably less accurate MP2 result as a lower limit (>217 kJ/mol). To prove these assumptions, we performed a complete basis set extrapolation³¹ utilizing the total energies obtained with the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets. The dimerization energies calculated with these extrapolated total energies of S_4^+ and S_4^{2+} [denoted CBSE(b,c) in Table III] never dropped by more than a few kJ/mol, so indicating that the cc-pVQZ basis set gives values close to the basis set limit.

We conclude from the above results that MP n ($n = 2, 3, 4$) theory is diverging in this case, and one has to employ more sophisticated levels of theory to describe the S_2^+/S_4^{2+} system adequately. Consequently, we also calculated the gas phase dimerization energy at the highly correlated CCSD and CCSD(T) levels and extrapolated the dimeriza-

tion energy to the complete basis set limit (DZ \rightarrow QZ,^{31,32} included in Table III). The best value obtained by using this procedure, i.e., 268.76 kJ/mol [CCSD(T)/CBSE(b,c)³¹], and the 265.74 kJ/mol calculated at the CCSD(T)/cc-pV5Z³² level, are very close to the dimerization energies as calculated by hybrid HF-DFT theory and flexible basis sets. These low values are also obtained by compound methods, which perform a predefined set of calculations and determine energies at various levels of theory allowing extrapolation to the correlation and basis set limit. Among the compound methods available within Gaussian94W,¹⁶ Peterson's complete basis set extrapolation CBS-Q¹⁹ and the Gaussian-2 theory²⁰ are reported to be the most accurate, as is demonstrated by the low mean average and maximum deviation from experiment when applied to the G2 molecule set²⁰ (CBS-Q: 3.3 and 15.9 kJ/mol, Gaussian-2: 5.0 and 21.3 kJ/mol for the computation of a total of 125 ionization potentials, proton affinities, atomisation energies, and electron affinities of second and third row molecules).^{19,20} Both employ MP4 and QCISD(T) as the highest levels of theory. A thorough description of the strengths and weaknesses of the compound methods can be found elsewhere.²⁶ The less accurate compound methods Gaussian-1, Gaussian-2(MP2), and CBS-4 were included in our studies for the sake of completeness, and the results are given in Table IV together with our other results. To test the reliability of CBS-Q and Gaussian-2 in the context of this problem, the ionization potential of S_2 was computed and revealed good agreement with experiment (CBS-Q: 909.9 kJ/mol, Gaussian-2: 895.2 kJ/mol, experiment: 902.7 ± 0.2 kJ/mol). When employed for the computation of the dimerization energy of the $2S_2^+/S_4^{2+}$ system, both methods give low values of 248 (CBS-Q) and 266 (Gaussian-2) kJ/mol, well within the limits as concluded from Table III and close to the CCSD(T) result of about 269 kJ/mol calculated at the extrapolated basis set limit. Owing to the substantially smaller basis sets and lower levels of theory employed, the dimerization energies computed by Gaussian-1 and CBS-4 are too high.

Inspection of the results in Tables II, III, and IV allows one to speculate that the true dimerization energy will still be lower than the best directly computed value of about 269 kJ/mol [CCSD(T)/CBSE(b,c)], for example, CCSD(TQ) extrapolated to the basis set limit would still lead to a further, albeit small, lowering of the dimerization energy. Therefore, we may conclude that the average CCSD(T), CBS-Q and Gaussian-2 dimerization energy of $(269 + 248 + 266)/3 = 261$ kJ/mol will be

TABLE IV. Computed Ionization Potential of S_2 and the Dimerization Energies of the $2S_2^+/S_4^{2+}$ System Including $d(S-S)$ [in (Å)] Using Various Compound Methods.

Level of Theory	S_2 $d(S-S)$	S_2^+ $d(S-S)$	IP of S_2 kJ/mol	S_4^{2+} (D_{4h}) $d(S-S)$	ΔU_{dim} kJ/mol
Experiment	1.889	1.824	902.7 ± 0.2	2.011(3)	—
Gaussian-1	1.920	1.868	894.2	2.065	303
CBS-4		1.870	911.4	2.066	281
Gaussian-2(MP2)	1.920	1.868	891.0	2.065	251
Gaussian-2	1.920	1.868	895.2	2.065	266
CBS-Q	1.939	1.870	909.9	2.066	248

close to the experimentally expected value. When the zero-point energies of S_2^+ and S_4^{2+} are included [from the B3LYP/6-311+G* geometries] and the total energies are corrected to the enthalpy at 298 K, the final dimerization *enthalpy* is lowered by an additional 3.63 kJ/mol, that is

$$\Delta_r H^{298}(2S_2^+ \rightarrow S_4^{2+}) \approx 257 \text{ kJ/mol}$$

The data obtained at many different levels of theory as given in Table I can now be understood. Because the dimerization energy is highly dependent on a large basis set using an electron correlated method, the basis set limit of the levels of theory used could never be reached. Therefore, all dimerization energies are too high. This is not true for the hybrid HF-DFT methods B3LYP and B3PW91, because they, in effect, bypass the need to treat the interelectron repulsion cusp. Both converge within the basis sets employed to a single value for the dimerization energy. The approximately 20 to 25 kJ/mol difference between the B3LYP level of theory near the basis set limit (e.g., B3LYP/aug-cc-pVTZ), and our best value of 261 kJ/mol (see above) arise as intrinsic errors of the Lee-Yang-Parr correlation functional. Although it is often accepted that there is no advantage in employing the B3PW91 rather than the more popular B3LYP hybrid functional, our experience (and that of one of our referees) tends to suggest that this is not always the case. When applied to the S_2^+/S_4^{2+} problem, the Perdew-Wang 1991 correlation functional performs better and gives essentially the same energies as our derived best value—provided they are used with a sufficiently large basis set [e.g., B3PW91/6-311+G(3df)]. This can be understood if one takes into account that Becke optimized his three-parameter exchange functional (B3)¹⁷ us-

ing the Perdew-Wang 1991 correlation functional (PW91)²⁷ by computing the properties of the G2 molecule set.

THE GAS PHASE DIMERIZATION ENERGY IN THE Se_2^+/Se_4^{2+} SYSTEM

The gas phase dimerization energies of the $2Se_2^+/Se_4^{2+}$ system at various levels of theory are summarized in Table V. Here, the energies of reaction vary from 169 to 241 kJ/mol if one neglects the uncorrelated HF/6-311G* result—much less than the span observed in the homologous sulfur system (v.s.: 232 to 522 kJ/mol). Compound methods are not available for structures containing selenium atoms within Gaussian 94W, so they cannot be used as a benchmark. However, the interpretation of the dimerization energies is the same as for the sulfur system, but basis set and correlation effects are much less pronounced. The maximum change is found in the MP2 calculations on the HF/6-311G* geometry [maximum deviation 34 kJ/mol going from the 6-311G* to the 6-311(2df) basis set; compared to 133 kJ/mol in the analogous sulfur calculations]. Hybrid HF/DFT theory has almost reached its basis set limit employing a 6-311+G* basis set, lowering the dimerization energy by just an additional 11 kJ/mol (B3LYP) or 1 kJ/mol (B3PW91) when changing to the largest basis set. MP2 overemphasizes correlation (as indicated by a low dimerization energy of 169 kJ/mol), somewhat corrected by MP3 and MP4. Summarizing all these trends, one can conclude an average gas phase dimerization energy of about 199 ± 20 kJ/mol [derived from the five best calculations in Table V: B3LYP, B3PW91, MP2, MP3, and MP4(SDQ) employing the largest basis set].

TABLE V.
Computed Dimerization Energies of the $2\text{Se}_2^+/\text{Se}_4^{2+}$ System Including $d(\text{Se—Se})$ [in (Å)] at Various Levels of Theory.

Level of Theory	Se_2^+ $d(\text{Se—Se})$	$\text{Se}_4^{2+} (D_{4h})$ $d(\text{Se—Se})$	ΔU_{dim} kJ/mol
B3LYP/6-311+G*	2.119	2.342	205.89
B3LYP/6-311+G(3d2f)//B3LYP/6-311+G*	2.119	2.342	195.30
B3PW91/6-311+G*	2.104	2.319	181.48
B3PW91/6-311G(2df)//B3PW91/6-311+G*	2.104	2.319	180.38
HF/6-311G*	2.060	2.276	317.60
MP2/6-311G*//HF/6-311G*	2.060	2.276	202.92
MP2/6-311G(2df)//HF/6-311G*	2.060	2.276	169.34
MP3/6-311G(2df)//HF/6-311G*	2.060	2.276	217.11
MP4(SDQ)/6-311G(2df)//HF/6-311G*	2.060	2.276	233.14
QCISD(T)/6-311G*//HF/6-311G*	2.060	2.276	241.16

S₂, S₂⁺ AND M₄²⁺ (M = S, Se) GEOMETRIES AT VARIOUS LEVELS OF THEORY

Experimental gas phase S—S bond distances are available for S₂ (1.889 Å)²⁸ and S₂⁺ (1.824 Å).²⁹ For S₄²⁺, X-ray single-crystal structure determinations show the square planar, *D*_{4h} symmetric cation in various AsF₆[−] and [(Sb₂F₄)(Sb₂F₅)(SbF₆)₅]^{2−} salts with S—S bond lengths that range from 1.975(5) to 2.015(2) Å.^{4,15} The crystal structure of S₄(AsF₆)₂AsF₃⁴ is well determined at low temperature, and has been corrected for thermal motions. The S—S bond lengths in this cation are the most accurate available and average to 2.011(3) Å. This compares well to the computed bond distances given in Table I. They mirror experimentally observed values within a few pm. However, the Hartree–Fock theory, lacking correlation, gives substantially shorter bond lengths compared with all correlated methods (shrinkage about 4–6 pm for S₂, 4–9 pm for S₂⁺, and 3–8 pm for S₄²⁺). All S—S distances computed by correlated methods are somewhat longer than the experimentally observed bond lengths. The higher the level of theory and the larger the basis set, the shorter is *d*(S—S) in the optimized structures [see Table II, e.g., MP2/6-31G* (1.939, 1.870, and 2.066 Å) vs. MP3/6-311+G* (1.912, 1.833, and 2.051 Å); B3LYP/6-311+G* (1.927, 1.844, and 2.072 Å) vs. B3LYP/aug-cc-pVTZ (1.913, 1.833, and 2.051 Å)]. Employing the B3PW91 level of theory together with the flexible 6-311G(2df) basis set gives the geometries closest to experiment [*d*(S—S) =

1.897, 1.819, and 2.027 Å vs. 1.889, 1.824, and 2.011(3) Å exp.]. This behavior can be attributed to the overestimation of the correlation in the less sophisticated wavefunctions.²⁴ As soon as the description of the correlation effects improves the bond distances shrink. S₄²⁺ is found in a rather shallow potential, such that changing *d*(S—S) from 2.072 Å to 2.000 Å only increases the energy by 8 kJ/mol (B3LYP/6-311+G*). This explains the difficulties in mirroring the experimentally observed bond lengths exactly with all but the best methods. The B3PW91/6-311+G* optimized geometries (1.914, 1.831, and 2.053 Å) resemble those computed at the MP3/6-311+G* (1.912, 1.833, and 2.051 Å), QCISD/6-311+G* (1.915, 1.840, and 2.055 Å), or B3LYP/aug-cc-pVTZ (1.913, 1.833, and 2.051 Å) levels of theory. This, and the very accurate geometries obtained with the 6-311G(2df) basis set again underline the strengths of this particular method for the 2 S₂⁺/S₄²⁺ system, because its computational requirement is substantially less than that needed by the other methods.

The *D*_{4h} symmetric Se₄²⁺ dication is found in various salts in the solid state, and exhibits an average Se—Se bond length of 2.284(4) Å^{21,22,30} (not corrected for thermal motions, which add approximately 1 pm). Computed Se—Se distances are given in Table V. All methods mirror the experimental values within a few pm. However, correlated methods tend to give longer Se—Se distances than found in experiment. Similar to the sulfur system, the Perdew–Wang 1991 gradient corrected correla-

tion functional²⁷ [$d(\text{Se}—\text{Se}) = 2.309$ (see below) and 2.319 \AA] performs better than the older Lee–Yang–Parr functional¹⁸ [$d(\text{Se}—\text{Se}) = 2.342 \text{ \AA}$], and gives bond distances that are closer to the experimental values.

Concluding Remarks

The prescription for modeling thermochemically accurate dimerization energies for the reaction $2 \text{S}_2^+ \rightarrow \text{S}_4^{2+}$ consists of selecting a method near the correlation and basis set limit. This is achieved best by using compound methods (e.g., Peterson's complete basis set extrapolation, Gaussian-2), the computationally very expensive CCSD(T) level extrapolated to the complete basis set limit or else by employing hybrid HF/DFT calculations with flexible basis sets. B3PW91 was the most economical level of theory found to be capable of yielding accurate energies and geometries. Reliable energies are computed at the B3PW91/6-311+G(3df)//B3PW91/6-311+G* level of theory. The inclusion of polarizing f -functions is crucial in the energetic description of these strongly delocalized ions. Applied to the given problem, $\text{MP}n$ ($n = 2, 3, 4$) perturbation theory performs moderately and diverges. The MP2 level of theory largely overestimates the effects of electron correlation in these species, and the MP3 and MP4(SDQ) methods underestimate this contribution. In the selenium case, the dependence on the level of theory and basis set employed is much less pronounced, presumably due to less electrostatic repulsion in the larger dicationic system (e.g., from 2.0 to 2.3 \AA widened (interatomic separation)). With hybrid HF–DFT methods (best: B3PW91) already the 6-311+G* basis set is sufficient to describe energetics and structure of Se_4^{2+} .

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